

# AB INITIO PREDICTIONS OF STRUCTURES AND DENSITIES OF ENERGETIC SOLIDS

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## ABSTRACT

We have applied a powerful simulation methodology known as *ab initio* crystal prediction to assess the ability of a generalized model of CHNO intermolecular interactions to predict accurately crystal structures and densities of various classes of explosives. 174 crystals whose molecules contain functional groups common to CHNO energetic materials were subjected to this methodology and include acyclic and cyclic nitramines, nitrate esters, nitroaromatics, and nitroaliphatic systems. The results of these investigations have shown that for 148 of the 174 systems studied the predicted crystal structures matched the experimental configurations; 75% of these corresponded to the global energy minimum on the potential energy surface. The success rate in predicting crystals with structural parameters and space group symmetries in agreement with experiment indicates that this method and interaction potential are suitable for use in crystal predictions of similar CHNO systems when the molecular configuration is known.

## 1. INTRODUCTION

A molecular simulation capability of particular importance in energetic materials development is that of *ab initio* crystal structure prediction. This type of calculation has the potential to significantly enhance and optimize the design and development of advanced energetic materials because it allows the prediction of a key property associated with performance of the material: its crystal density. The ability to predict the crystal density will allow a designer to assess detonation or gun performance without the need to synthesize the material. In this manner, candidates with densities that will produce less-than-satisfactory performances can be eliminated from further consideration before actual resources are expended on synthesis. Therefore, this important methodology is considered to be a key computational tool in the development of advanced energetic materials research.

In addition to allowing a materials designer to rapidly examine a wide variety of notional candidate materials for applications in which crystal morphology or density is a critical indicator of behavior, activity and performance, the method can be used to assess molecular simulation models that might be used in other types of molecular simulations (i.e. molecular dynamics).

The success of the method is dependent on the quality of the model used to describe intermolecular interactions among the atoms in the crystals. The model used in this study is a generalized CHNO intermolecular interaction potential developed for use in other types of molecular simulations (Sorescu et al., 1997). This model, denoted as the SRT model after its original authors, has already been subjected to a series of molecular simulation studies in which its ability to predict properties of a variety of molecular crystals has been evaluated (Sorescu et al., 1998a, 1998b, 1998c, 1999a, 1999b). Although the SRT model appears to be a promising model for use in molecular simulation of CHNO molecular crystals, increasingly rigorous assessments should be performed to establish the limits of the model's capabilities and provide information for refinement. Particularly, it is important to establish whether such a potential is able to reproduce the crystal structure and the corresponding lattice energy known from experimental data and also to predict the crystallographic symmetry without its prior knowledge. The study presented here provides such an evaluation. In this work, we have subjected a series of CHNO crystals that are representative of different classes of explosives to *ab initio* crystal structure prediction using the SRT interaction potential, in order to appraise the performance of this method and model in generating hypothetical crystal structures that are consistent with those observed experimentally. We have attempted to make this analysis comprehensive by considering a large number of chemical systems of interest for energetic materials applications. In particular, in this work we have considered compounds containing nitramines, nitrate esters, nitroaliphatics, nitroaromatics, and furoxans.

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## 2. EXPERIMENTAL DATA USED IN THE STUDY

The structural data of the molecular systems considered in this study were obtained from the Cambridge Structural Database (CSD) (Allen, 2002). No modifications to the experimental structures were made. The main categories of compounds used were species having nitro groups attached to carbon (denoted as nitroaliphatic or nitroaromatic), nitrogen (nitramine), or oxygen (nitrate esters). Additionally, a few furoxan systems were considered. Within this paper, systems will be referred to by their CSD entry identifier (*refcode*). Structures were eliminated from consideration for this study if: 1) The space group could not be treated by the software used in the calculations, MOLPAK (Holden et al., 1993; Busing, 1981; Cromer et al., 1987). We did not exclude crystals with space groups that were alternate settings of those that could be treated by the version of MOLPAK used in this study. 2) The systems contained atoms other than C, H, N and O. 3) The systems contained solvent molecules. 4) There is more than one molecule in the asymmetric unit. 5) Those systems in which the asymmetric unit contains only part of the molecule and no C2 rotation axis or center of inversion exist among the symmetry elements of the crystal. However, when such symmetry elements are present the corresponding crystals can be considered for MOLPAK simulations. 5) Fractionals for some or all of the non-H atoms were not available. 6) Systems that have disordered atomic positions or have crystallographic R-factors greater than 11%.

This search, which was not exhaustive, resulted in the identification of 174 molecular crystals that represent our working database to be subjected to ab initio crystal prediction. Information about these, including full chemical name, CSD *refcode*, chemical formula, space group, temperature at which measurements were taken, and reported R-factors are given in Rice and Sorescu (Rice and Sorescu, 2004).

## 3. INTERMOLECULAR POTENTIAL

The PES is represented by a very simple model for use in rigid-molecule simulations; its form is a simple atom-atom exponential-six plus Coulombic potential. The partial charges used in the Coulombic interaction terms were determined by fitting atom-centered partial charges to a quantum-mechanically determined electrostatic potential for a single molecule whose structure corresponded to that in the crystal at ambient conditions. The remaining exponential-six parameters were adjusted to reproduce the experimental structure of the RDX crystal at ambient conditions (Sorescu et al., 1997).

## 4. COMPUTATIONAL METHOD

### 4.1. The MOLPAK/WMIN Crystal Structure Prediction Method

In our study, we have used the ab initio crystal structure prediction software MOLPAK/WMIN (Holden et al., 1993; Busing, 1981; Cromer et al., 1987), developed with an emphasis on density predictions of energetic materials. A key assumption in the MOLPAK/WMIN procedure is that of closest packing of the molecules in the crystal; the procedure attempts to identify structures with the highest densities. The MOLPAK portion of the calculation generates numerous candidate crystal structures of minimum volume for molecular coordination geometries observed in the most common space groups. MOLPAK considers 29 coordination geometries for the triclinic ( $P1$ ,  $P\bar{1}$ ), monoclinic ( $P2_1$ ,  $P2_1/c$ ,  $Cc$ ,  $C2$ ,  $C2/c$ ) and orthorhombic ( $Z=4$ ,  $P2_12_12$ ,  $P2_12_12_1$ ,  $Pca2_1$ ,  $Pna2_1$  and  $Z=8$ ,  $Pbcn$ ,  $Pbca$ ) space groups. A subset consisting of the most dense candidate crystals are subjected to further refinement through full energy minimization using the program WMIN (Busing, 1981). The steps in the procedure are:

1. The Cartesian coordinates of the three-dimensional molecular model that is to be used in building the candidate crystals (hereafter referred to as the “test molecule”) are specified. The centroid of the test molecule is located at the origin of the hypothetical crystal. The orientation of the molecule is given by a set of Euler angles. In this study, the arrangement of the atoms in the molecule corresponds to that of the crystal molecular structure, as reported in the CSD (Allen, 2002). An alternate method of determining the coordinates of the test molecule is through quantum mechanical prediction.

2. An initial packing arrangement is obtained by surrounding the test molecule with a coordination sphere containing other molecules. The contents and three-dimensional structure of the sphere are dependent on the crystalline space group symmetry. The definitions of the various coordination spheres used in a MOLPAK calculation were obtained from detailed analyses for a large number of organic crystal structures (Holden et al., 1993). The analyses showed that the most probable number of molecules in the coordination sphere is 14, and that specific “patterns and sub-patterns” were apparent in the three-dimensional structure of the coordination spheres (Holden et al., 1993).

3. Adjacent molecules in the coordination sphere are then systematically moved in small steps toward the centrally-located test molecule. At each step, the potential energy of the “crystal” is calculated. This continues until a repulsion criterion is met. Once this criterion is met, the

packing procedure stops, and the volume, crystallographic parameters and Eulerian angles that describe the orientation of the test molecule are stored.

4. The test molecule is then reoriented about only one of the Eulerian axes by  $10^\circ$ , and the packing procedure (steps 1-3) is repeated until the entire Eulerian space is sampled. Rotations in  $10^\circ$  steps about the three Eulerian axes will result in the generation of 6,859 ( $19^3$ ) orientations and hypothetical crystal structures for each of the possible space group/coordination sphere combinations.

5. After the  $\sim 7000$  structures were generated for each coordination sphere geometry, they are ranked according to density. The 25 most dense structures are subjected to full energy minimization, where minimization is performed with respect to the crystallographic parameters. The energy minimization is space-group symmetry restricted (i.e., the space group symmetry is conserved throughout the minimization), and performed using the code WMIN (Busing, 1981).

At the completion of the energy minimizations of the 25 most dense hypothetical crystals generated for each of the 29 space group/coordination-sphere geometries, the user has the information needed to identify the “correct” crystal structure according to his specific criteria (e.g. lowest lattice energy or highest density [Lommers et al., 2000]). During energy minimizations some of the hypothetical crystals can converge to the same local minimum on the PES. However, identical crystals have not been eliminated in the analyses reported hereafter.

The MOLPAK/WMIN procedure proceeds under the assumption that all important regions of configuration space are adequately sampled and that the interatomic interactions are sufficiently accurate to describe packing and lattice energies. Unfortunately, we found that in some cases, the MOLPAK/WMIN procedure did not result in the identification of the experimental structure. For those cases, a second MOLPAK/WMIN series of calculations were performed in which the test molecule was reoriented about each of the Eulerian axes in increments of  $5^\circ$ , resulting in the generation of 50,653 ( $37^3$ ) orientations and a corresponding larger number of hypothetical crystal structures. For a number of structures, the increased resolution of the grid led to successful identification of the corresponding experimental structures.

#### 4.2. METHOD OF COMPARISON OF STRUCTURES

The comparison of crystallographic structures predicted using the MOLPAK/WMIN codes with

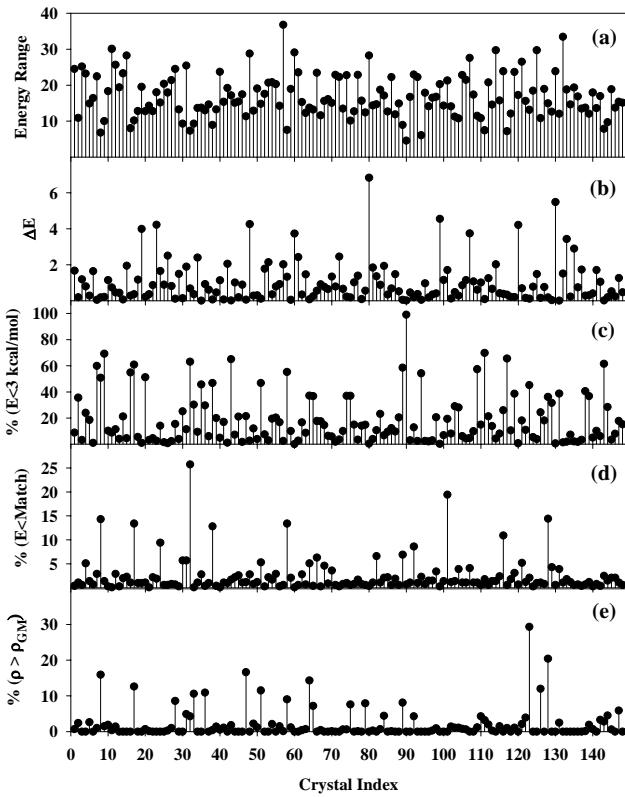
experiment was accomplished in a series of steps. The first step is the comparison of the reduced cell parameters obtained from MOLPAK calculations with the corresponding experimental values. The MOLPAK crystal with reduced cell parameters that most closely agree with experimental values is identified as a potential match.

A more rigorous comparison of crystals has been performed to check that not only the lattice parameters are in agreement with experimental values but also that the arrangement and orientation of molecular systems inside the unit cell resemble the experimental situation. The first step of this portion of the assessment is the generation of the experimental unit cell and a MOLPAK supercell consisting of 125 unit cells ( $5 \times 5 \times 5$  unit cells). Next, the experimental unit cell and MOLPAK supercell are translated such that the mass centers of the central molecule of the MOLPAK supercell and one of the molecules in the experimental unit cell are located at the origin. Using the procedure described by Kearsley (Kearsley, 1989), the MOLPAK supercell is then rotated about the origin such that the central molecule of the MOLPAK supercell is superimposed onto the experimental molecule. Since the molecular structures used in the MOLPAK calculations are exactly the same as those in the experimental unit cells, the Kearsley procedure will result in a perfect superposition of the MOLPAK and experimental molecules. At this point, the molecules in the MOLPAK supercell that correspond to each of the remaining equivalent molecules in the experimental unit cell are identified by minimizing the root-mean-square (rms) deviation of distances between the two sets of molecules. Once the MOLPAK unit cell that most closely resembles the experimental unit cell is obtained, the MOLPAK and experimental unit cells are shifted such that the mass centers of both cells are located at the origin. The Kearsley procedure (Kearsley, 1989) is then applied using all molecules within both unit cells, to obtain optimum superposition of the MOLPAK unit cell onto the experimental cell. Locations of mass centers and orientations of all molecules in both experimental and predicted unit cells are calculated and compared. Orientations of the molecules are described in terms of the Euler angles used to rotate the Cartesian coordinate axes onto those of the principal axes of each molecule. Finally, a visual comparison of the superimposed unit cells is performed to confirm that the MOLPAK unit cell resembles the experimental cell.

#### 5. RESULTS

Several types of data are extracted from the ab initio MP results: First, we determine the lattice energies of the global minimum (GM) and that of the structure which represents the match of the corresponding experimental configuration. This last type of structure will be denoted in the following as “the match”. In the majority of cases

the global minimum coincides with the match to experiment and as a result the two energies are identical. We also calculated the energy gap between the global minimum and the next local minimum with energy closest to the GM determined from the entire set of hypothetical crystal structures of a particular system. For each particular case the energetic range sampled by the corresponding hypothetical crystal structures was determined. We also determined the percentage of crystals with energies smaller than that of the match structure and with energies within 3 kcal/mol from the GM. Finally, we determined the percentage of crystals with energies within 3 kcal/mol of GM and with densities greater than the one determined for the structure at the global minimum. All of this information is illustrated in Figure 1.



**Figure 1** (a) The energy range of the hypothetical crystals generated for each system; (b) The energy gap  $\Delta E$  between the global minimum (GM) and the local minimum with energy closest to the GM; (c) Percentages of systems that are within 3 kcal/mol of the GM; (d) Percentages of systems that have lattice energies lower than the the structure that matches the experiment; (e) Percentages of systems with densities higher than that of the GM. The crystal indices for each frame correspond to those assigned to the various chemical systems listed in Table 2S of Sorescu and Rice (Sorescu and Rice, 2004). The energy units are kcal/mol.

The ranges of lattice energies relative to the GM for the various hypothetical crystals are represented in Figure 1(a). It can be seen that there is a relatively large spread of the energetic ranges with values between 4.6 kcal/mol to nearly 40 kcal/mol. It has been recommended that structures with lattice energies that are more than 3 kcal/mol higher than that of the GM should not be considered as probable structures (Motherwell et al., 2002); therefore, for those systems in which the energy ranges are quite large, the higher-energy crystals can be discarded from consideration. Furthermore, it has been proposed that for those cases in which the lattice energy of the match to experiment is the GM, a significant energy gap between the GM and all other crystals indicates “a readily predicted robust crystal structure” (Beyer et al., 2001). The corresponding energy gaps obtained in our simulations are presented in Figure 1(b). As indicated by this figure the gap energies have values below 2 kcal/mol for the great majority of crystals investigated indicating the presence of closely spaced local minima in the region of the GM. Also, as evident Figure 1(b), there are several cases in which the hypothetical crystals have lattice energies that are almost equal to the GM, even though upon inspection, the crystal parameters were often quite dissimilar (e.g. different space groups, different orientations of the molecules within the unit cell).

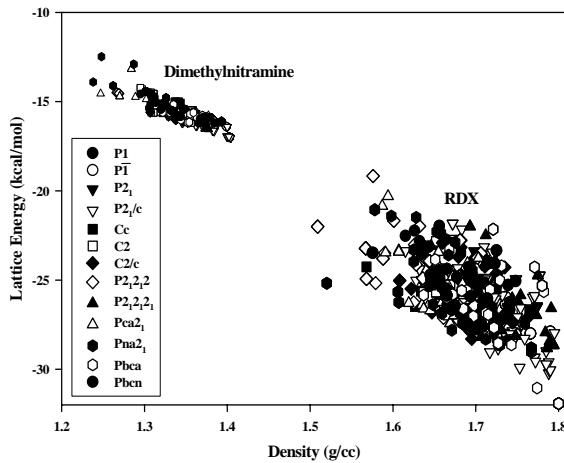
A similar finding emerges from the analysis of the data illustrated in Figure 1(c) where the percent of hypothetical crystals with lattice energies within 3 kcal/mol of the global minimum is represented. Indeed, it can be observed that for many systems a large number of the hypothetical crystals are distributed in a relative narrow energy window above the GM.

As shown in Figure 1(d) where the percentages of crystals that are lower in energy than the matches are given, the hypothetical crystal selected as the match to the experimental structure is, in most cases, among the lowest-energy crystals generated in the MOLPAK/WMIN procedure.

We have investigated whether crystalline polymorphs with higher densities have correspondingly lower lattice energies; the corresponding results are presented in Figure 1(e). In this figure we represent the percentage of hypothetical crystals with densities greater than that of the structure corresponding to the GM. As indicated in Figure 1(e), we observe that in majority of analyzed cases, systems having the highest density correspond to the GM while a relatively small number of crystals have densities in excess of that of GM.

One of the systems having a GM with structural parameters in good agreement with experiment and with a significant energy gap between the GM and all the other hypothetical crystals is CTMTNA (RDX, Cyclotrimethylene-trinitramine). In this case there is also a moderate range of spread of energies (12.75 kcal/mol)

for various hypothetical structures. The predicted densities and the corresponding lattice energies for all local energy minima identified are shown in Figure 2. In this case, the difference in energy between the GM and all the other crystals is 0.87 kcal/mol. The next local minimum above the GM has the same space group symmetry as the experimental structure and has crystallographic parameters that deviate from experiment by only a few percent. However, the rms rigid body rotational and translational displacements for this structure are large, and the pictorial representations of the hypothetical crystal superimposed onto the experimental unit cell confirmed that this higher-energy crystal could not be considered as a good match for this system.



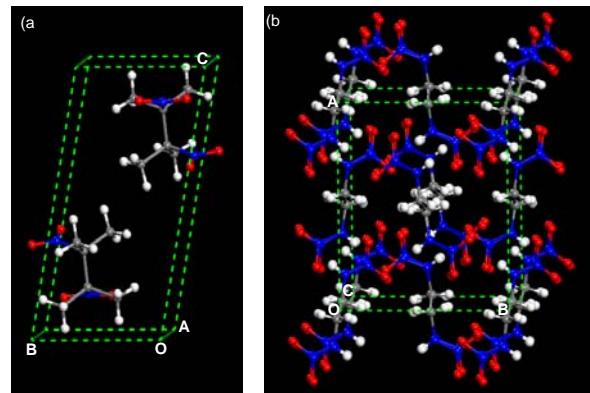
**Figure 2** Lattice energies versus densities of hypothetical crystals of METNAM22 and RDX generated by ab initio crystal prediction methods. Crystalline space groups in which minimizations were performed are denoted by the symbols defined in the legend.

For the RDX system, only 4.6% of the crystals have energies within 3 kcal/mol of the GM, and as a result of lattice minimization 48% of these (namely 2.2% from the total number) have converged to the same energy minimum (the GM) after minimization. For this crystal it has also been found that the structure corresponding to the GM has also the highest density among the series of hypothetical crystals. In contradistinction to the RDX case we have also found several situations where the lattice energies of the hypothetical crystals are almost equal to the GM despite significant differences in the symmetries and crystallographic parameters of these structures. Such a case is the METNAM22 crystal (Hexadeutero-N,N-dimethyl-nitramine,), also illustrated in Figure 2. In this case the range of lattice energies of the predicted hypothetical crystals is 4.5 kcal/mol while 99% of the hypothetical crystals have lattice energies within 3 kcal/mol of the global minimum (GM). The GM for METNAM22 is identified as the Match to the experimental crystal having the monoclinic  $P2_1/c$

symmetry. The local minimum with energy closest to the GM identified by MOLPAK/WMIN procedure has space group symmetry  $P\bar{1}$  and is separated by only 0.02 kcal/mol from the GM. Symmetry-constrained normal mode analyses confirmed that these energy minima are different.

### 5.1. Identification of Matches to Experimental Crystals

In most cases, the best match of MOLPAK predictions to experiment is easily determined and the superposition of the MOLPAK match to experiment is so good that visually, the molecules are indistinguishable. Such a case is, for example, the BECJEY (2,3-Dimethyl-2,3-dinitrobutane) crystal represented in Figure 3a. However, there were a few cases in which the molecular orientations and mass positions within the cell had larger differences from experiment. Such an example is illustrated in Figure 3b for the case of the DNEDAM crystal.



**Figure 3** Pictorial views of the unit cell structures predicted by MOLPAK superimposed onto the experimental unit cells for the (a) BECJEY and (b) DNEDAM crystals. The cell vectors correspond to the experimental values.

The MOLPAK/WMIN calculations generated crystals that matched the experimental structure for 148 of the 174 systems studied (85%). Eight of the 148 matches were found only after performing a second set of calculations in which the test molecule is reoriented about each of the Eulerian axes in increments of  $5^\circ$  during the MOLPAK portion of the calculations. 75% (111) of the 148 matches have the lowest lattice energy of all candidate crystals generated in the MOLPAK/WMIN procedure.

Another point we have investigated in this study is whether the aforementioned statistics on the capability of the MOLPAK/WMIN procedure to identify crystal structures consistent with experiment are dependent on the chemical classes of CHNO crystals included in this study, i.e. nitramines, nitroaliphatics, nitroaromatics and nitrate esters. In performing this analysis we need to point out

that several systems have been included in more than one category since many of them have multiple  $\text{NO}_2$  groups that are attached to different atom types. For example, the ENPROP (Ethyl 3-nitro-2-nitro-3-(4-nitrophenyl)-propionate) crystal has  $\text{NO}_2$  groups attached to oxygen, an aliphatic carbon and an aromatic carbon. Therefore, in the subsequent analyses, ENPROP is categorized as a nitrate ester, a nitroaliphatic and a nitroaromatic system.

**Nitramines:** This category contains 77 crystals that were subjected to ab initio crystal prediction. Of these, 84% (65) were identified as a match to experiment by the MOLPAK/WMIN procedure. 78% (51) of the crystals identified as matches to experiment correspond to the global energy minimum.

**Nitroaliphatic:** 85% (56) of the 66 candidates in this category were identified as matches to the experimental systems by the MOLPAK/WMIN procedure; of these, 73% (41) correspond to the global energy minimum.

**Nitroaromatic:** 27 out of 29 of the systems in this category (93%) were identified as matches to experiment. Of these, 78% (21) correspond to the global energy minimum

**Nitrate Esters:** Of the 33 crystals in this category, 85% (28) were identified as matches to the experimental crystals; 79% of these (22 out of 28) correspond to the global energy minimum.

Separate analyses were not performed for systems that could be categorized as furoxans or systems containing azido or nitroso groups, due to the small numbers of these types of systems studied. The above results indicate that in terms of identification of the experimental structure, the method and SRT model behave fairly consistently across all categories investigated with a success rate of about 85% for the nitramine, nitroaliphatic and nitrate ester categories and an even slightly higher success rate for the nitroaromatic class of 93%. This consistency is also observed with regard to the percentages of the identified matched systems corresponding to the global minimum. In this case the success rate ranges from 73% to 79%.

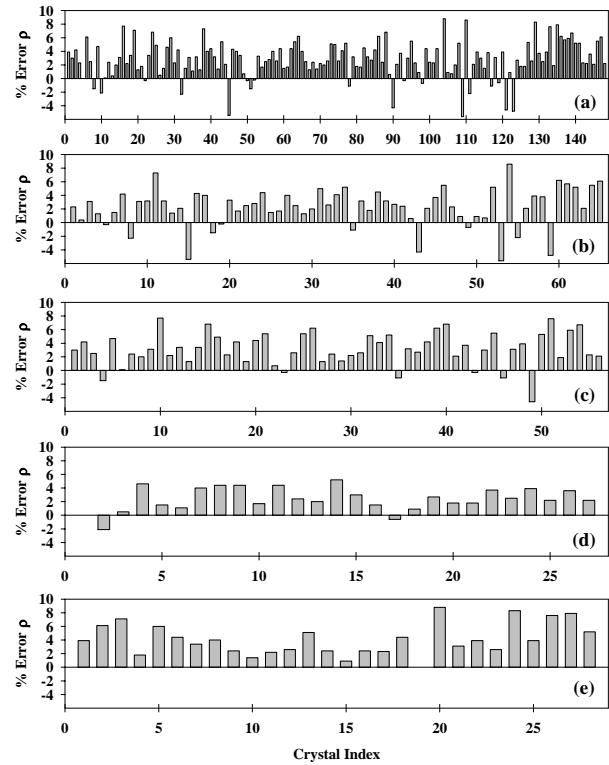
For the 37 matches that did not have the lowest lattice energy among the possible candidates, all but six had lattice energies within 1 kcal/mol of the global energy minimum. The largest difference in energy between the match to experiment and the structure with lowest lattice energy is for PERYTN01 (Pentaerythritol tetranitrate, 2.86 kcal/mol). This particular result could be indicative of deficiencies in the SRT force field for this system. However, for this system, no R factor was recorded; so it is also possible that the structure is not well characterized at the experimental conditions.

An additional analysis was performed to determine whether failures of the search method clustered into

particular space groups. For the most part, no clustering of failures occurred in any particular space group. For each individual space group analyzed by MOLPAK we determined that 80 to 100% of the systems with that space group produced matches to the experimental structures. An exception from this statistics was seen for the case of Pca21 crystal symmetry which had a success rate of 50%. However, in this case there were only four systems with this space group symmetry.

## 5.2. Structural Predictions.

The MOLPAK/WMIN predictions of the densities for crystals identified as best matches to experiment are illustrated in Figures 4.



**Figure 4** Calculated percentage errors between the predicted and experimental values of the densities for (a) the entire set of crystals; (b) nitramine crystals; (c) nitroaliphatic crystals; (d) nitroaromatic crystals; and (e) nitrate ester crystals. The crystal indices for each frame correspond to those assigned to the various chemical systems listed in Table 3S of Rice and Sorescu (Rice and Sorescu, 2004).

Figure 4(a) shows the percent deviation in density of the MOLPAK predictions compared to experimental values for the entire set of molecules. Overall, the MOLPAK densities are overestimated on average by 2.8%, and have a rms deviation of 3.9%. Also, in the great majority of cases, namely 131 out of 148, the predicted

crystal densities were found to be larger than the corresponding experimental values. This is not surprising, since the MOLPAK/WMIN predictions reflect simple energy minimizations that do not include thermal effects, and the majority of the crystal structural parameters were determined at room temperature. Earlier NPT-MD simulations for a few of the systems studied herein predicted expansion of the lattice (i.e. a decrease in density) when thermal effects are included (Sorescu et al., 1997, 1998a, 1998b, 1999a). Therefore, the MOLPAK/WMIN results should be considered as upper limits to predictions of density, assuming that no unusual thermal expansion behavior exists.

The percent differences in density between predictions and experiment for the four categories of CHNO crystals analyzed in this study are illustrated in Fig. 4(b)-(e). The nitroaromatic category has the smallest rms deviation of predictions of density from experiment (2.9%), and the nitrate ester class had the largest (4.7%). The rms deviations of the predictions of density from experimental values for the nitramine and nitroaliphatic classes are 3.6 and 4.0%, respectively. Average percent deviations of density between the MOLPAK/WMIN predictions and experiment are 2.3, 3.1, 2.3 and 4.1% for the nitramine, nitroaliphatic, nitroaromatic, and nitrate ester classes, respectively.

The results indicate that for the majority of the crystals, the predicted lattice dimensions are smaller than experiment. The average percent differences for the cell edge lengths  $a$ ,  $b$  and  $c$  are all -1%, while the corresponding rms deviations of percent differences are 2.2, 2.2 and 2.1%, respectively. Since the symmetry of the crystals is constrained during the MOLPAK/WMIN calculations, orthorhombic and monoclinic systems have some or all cell angles fixed at 90° and were not allowed to vary during the packing/minimization procedure. Thus, these angles were not included in the distribution of absolute differences in predictions of cell angles from experimental values. The total number of non-fixed cell angles used in the distribution is 122. Among these about 88% of cell angles deviate from experiment by no more than 2°.

Regarding molecular orientation, the rms rigid-body rotational displacement and translational displacement after minimization for the entire set of crystals are 1.9° and 0.07 Å, respectively. The rms translational displacement for each of the nitramine, nitroaliphatic, nitroaromatic and nitrate ester classes is 0.07 Å. The corresponding rms rigid-body rotational displacement for same four categories, are 2.1, 1.8, 2.0 and 1.6°, respectively.

### 5.3. Problem cases

We have indicated in previous sections that the MOLPAK/WMIN procedure in conjunction with the SRT potential was able to match the experimental structure for 148 out of 174 systems studied. In this section we focus our efforts on possible sources of failure for the remaining 26 crystals. Particularly, in an attempt to determine whether the failure to identify the 26 of the 174 crystals was due to inadequacies in the SRT intermolecular interaction potential or in the search method, we performed geometry optimizations of the 26 crystals using the experimental crystals as initial structures in the MP calculations. Each calculation resulted in convergence to a local energy minimum and the corresponding crystal structure was superimposed on the experimental structure in the manner described in Section 4.2. Although there are notable disagreements in the predicted crystallographic parameters and molecular orientations with experiment, the predicted crystals resemble the experimental systems. In all cases, the predicted crystal densities were found to be smaller than the corresponding experimental values and on average underestimated the experimental values by 2.9%. This is in contrast to the results for systems identified through the MOLPAK procedure; in those cases, 89% of the systems had densities that were larger than experiment. The rms deviation of the density for these problem case crystals is 3.6%. Average percent differences for the cell edge lengths  $a$ ,  $b$  and  $c$  are -2.8, -2.5, and -2.8%, respectively while the corresponding rms deviations of percent differences are 4.3, 3.4 and 5.0%, respectively. The rms rigid-body rotational and translational displacements after minimization for this set of crystals are 3.6° and 0.13 Å. Overall, these results indicate that the SRT potential did a poorer job of representing these systems. Two systems were particularly poorly described by the SRT potential: NOGUNA01 (N-Methyl-N-nitroso-N'-nitroguanidine) and JIHVEB [(E)-Acetonitrolic acid]. For example, we have seen deviation of the cell edge lengths as high as 19.7% for NOGUNA01 and 10.76% for JIHVEB.

Beside deficiencies of the potential used in simulation of these crystals we note that another reason why some of the searches might have been unsuccessful is due to the existence of several local minima on the potential energy surface landscape. As a result, optimization of one of the candidate crystals generated during the search procedure might be prevented from reaching the GM or the local minimum corresponding to the experimental crystal due to convergence to one of the other local minima. In such an instance, the identification of a local minimum corresponding to the experimental structure is precluded. Beyer, Lewis and Price (Beyer et al., 2001) have suggested that the search procedure is flawed for those cases in which a local minimum with structural parameters close to experiment exists but which is not found during the search procedure (Beyer et al., 2001; Lommerse et al., 2000). Our results have clearly demonstrated that for the problem cases, there are several local minima with structural

parameters significantly different from those of the experimental structure. Since the direct minimization of the experimental structure for each of the problem cases resulted in convergence to a local minimum with structural parameters resembling experiment, the failure to identify these minima in the MOLPAK/WMIN procedure suggests that the search procedure is not fully adequate for these cases.

## 6. SUMMARY AND CONCLUSIONS

A total of 174 CHNO crystals for which experimental crystallographic information is available were subjected to ab initio crystal prediction using the MOLPAK/WMIN suite of software (Holden et al., 1993; Busing, 1981) and the Sorescu-Rice-Thompson (SRT) interaction potential for CHNO crystals (Sorescu et al., 1997). The systems under study consist of nitramine, nitroaliphatic, nitroaromatic and nitrate ester molecules and included a variety of acyclic, monocyclic and polycyclic/caged species. The calculations produced 148 crystals whose crystallographic parameters and molecular configurations matched those of the experimental counterpart. Of these, 75% corresponded to the global energy minimum on the potential energy surface. Predicted structural parameters of the matches were in good agreement with experimental values; predicted densities were higher than experiment by less than 3% on average, and cell edge lengths deviated from experiment on average by no more than -1%. Rigid body rotational and translational displacements had rms deviations from experiment of 1.9° and 0.07 Å, respectively.

For each of the chemical CHNO classes studied in this work, namely nitramines, nitroaliphatic, nitroaromatic and nitrate esters, we found similar statistics regarding identification of crystal and structural parameters. A slightly higher percent deviation of density from experiment was found for the nitrate ester class. The uniformity of the statistics for the four categories of CHNO crystals that were identified in the MOLPAK/WMIN procedure indicates that the SRT interaction potential is transferable among these classes of compounds. Consequently, this assessment provides a level of confidence in the SRT model when applied to these classes of CHNO compounds. The overall good performance of the MOLPAK/WMIN procedure and SRT potential in identifying the experimental systems and producing relatively good agreement with structural parameters for 85% of the systems studied demonstrates that both the model and method are reasonable to use in ab initio crystal predictions of similar CHNO systems when the molecular configuration is known.

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